Alkylating Refinery Grade Propylene

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Introduction

Refinery grade propylene (propylene/propane mix) is produced in Fluid Catalytic Cracking and Coking. The propylene in this stream can be combined with isobutane in an alkylation unit to yield a high-value gasoline blending component (alkylate). Alternatively, this material is sold, where it is often fractionated in an on-purpose facility to yield high-purity propylene that is subsequently used to manufacture a variety of petrochemicals including polypropylene, cumene, isopropanol, acrylonitrile, propylene oxide and epichlorohydrin.

There has been a significant shift from naphtha to ethane as feed to North American ethylene units because of the rise in production of natural gas liquids (NGLs) co-produced with shale gas and condensates. This has resulted in a reduction in the yield of co-product propylene from the ethylene units. A number of new propane dehydrogenation units have been built or are in the development process to alleviate this shortage. The increased volume of NGL production has also increased the supply of isobutane. This, combined with a ready supply of propylene, suggests that alkylation of propylene may have favorable economics.

The focus of this paper is to assess the feasibility of modifying an existing alkylation unit to process either refinery-grade or high-purity propylene. Case study results are presented where the modifications needed to revamp an existing 10,000 BPSD butylene sulfuric acid alkylation unit to handle either refinery- or polymer-grade propylene are identified. The analysis includes an estimate of the capital cost of the required revamp scope and the resulting economics based on the relative value of propylene as alkylation unit feed compared to that of refinery- or polymer-grade propylene product.

Refinery Alkylation

Refinery olefins that can be used as feed to alkylation units consist of mixtures of propane/propylene (PPs), butane/butylene (BBs) or amylenes, which are a mixture of C_5 saturates and olefins. Many sulfuric acid alkylation units use the DuPont® STRATCO sulfuric acid alkylation technology (See Figure 1). Olefin feed and make-up isobutane are combined with recycle isobutane from the distillation and refrigeration sections, cooled by heat exchange with net effluent from the suction trap, and fed to the shell side of the Contactor™ reactors, where olefins and isobutane are chemically combined to form alkylate, which consists mainly of highly branched isoparaffins. In the Contactor reactor, the feed and a large excess of isobutane are intensively mixed with sulfuric acid by a high-shear impeller that disperses the hydrocarbon and acid into an emulsion that circulates at a high rate over the tube bundle. The contents of the Contactor reactor are kept in the liquid phase to maximize hydrocarbon availability for the reaction. The hydrocarbons, now consisting of isobutane and alkylate with normal butane and a small amount of propane from the feed, are separated from the acid in acid settlers located above the contactors. Acid is returned to the contactors by gravity.

The hydrocarbon effluent from the acid settlers is partially vaporized at low pressure in the tube side of the Contactor reactors. This provides refrigeration to remove the exothermic heat of reaction and keep the contactor temperature in the optimum range.

The vapor and liquid phases in the effluent are separated in a large horizontal vessel called the suction trap. The vapor is then compressed and condensed in the refrigeration section. Condensed refrigerant, consisting mostly of isobutane, is flashed at low pressure in the flash drum (usually combined with the suction trap) from which cold liquid is recycled to the contactors. Flash-drum vapor combines with the suction-trap vapor as suction to the refrigeration compressor. The propane present in the feeds is removed from the refrigeration loop by feeding a slipstream of the condensed refrigerant to a depropanizer system.

Reactor effluent from the suction trap, containing the alkylate product, is treated to remove small quantities of free acid, alkyl sulfates and di-alkyl sulfate reaction byproducts in the effluent treatment section.

The distillation section recovers recycle isobutane and separates the remaining reactor effluent into normal butane and alkylate products. In some units, the normal butane product is recovered as a side draw from the deisobutanizer. Alternatively a separate debutanizer column, which provides better control over n-butane product purity and alkylate RVP, can be used. In this paper, a separate debutanizer column is utilized.

Case Study Description

A base case design including a preliminary process flow diagram (Figure 1), heat and material balance and sized equipment list was developed for a notional sulfuric acid alkylation unit that produces 10,000 BPSD of alkylate from FCC butane-butylene (BB) feed. Incremental isobutane supply beyond that contained in the BBs is from refinery saturate gas plant butanes and purchased high-purity isobutane. Other base case parameters are outlined in Table 1.

Table 1

Contactor Temperature	**°F**	**49**
Isobutane Consumption	BPSD	6180
Recycle Isobutane Purity%	vol %	85
IC4 / Olefin Ratio	Vol/vol	7.8
Total Heat Removal	MMBtu/hr	29.47
IC4 LV% in Contactor Effluent	vol %	65.8
Tube Side Temp In	°F	32
Tube Side Temp Out	°F	32.1
LMTD	°F	16.9
Contactor UA	Btu/hr-°F	1,736,000

Table 1

No. of Contactors		4
No. of Settlers		2
Total Ht. Transfer Area	ft^2	40280
Required 'U'	Btu/hr-°F -ft^2	43.1
n-Butane in Butane Product	Vol %	90
Isobutane in Propane Product	Vol%	1.6
Alkylate RVP	psia	3.7

The refinery butylene stream composition is listed below.

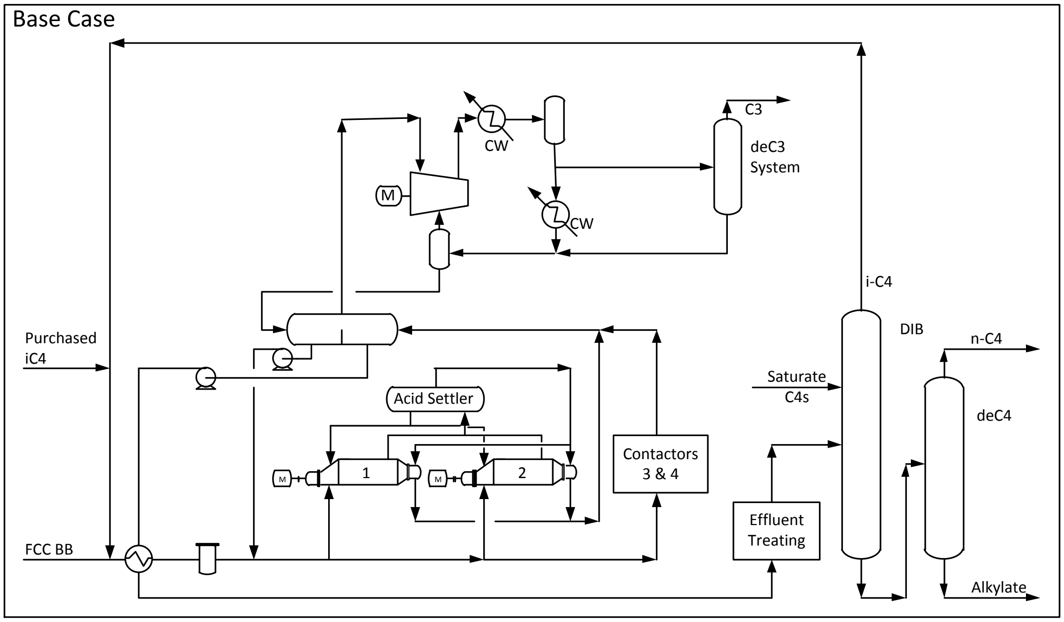
Component	**Vol%**
C3/C3=	0.9%
C4=	51.1%
iC4	34.0%
nC4	12.1%
C5/C5=	1.9%

The refrigeration compressor is a motor-driven centrifugal compressor operating at constant speed using suction throttling for control. Compressed refrigerant vapor is condensed in a single step (total condenser). An economizer is used to reduce the compressor size and power consumption by flashing recycled refrigerant liquid at an intermediate pressure.

The distillation section consists of a deisobutanizer (DIB) reboiled with 50 psig steam and a separate debutanizer reboiled with 150 psig steam. Both employ air-cooled condensers.

A depropanizer column is used to remove propane from the refrigeration loop. Refrigerant and depropanizer condensers are water cooled. The depropanizer reboiler is heated with 50 psig steam.

Figure 1



Two revamp cases feeding either refinery grade-propylene (PP) or purchased polymer-grade propylene were considered. Table 2 summarizes the olefin charge rates for the base case and two study cases.

Table 2 – Feed Rates

Case	Base	Case 1	Case 2
Refinery Mixed Butane/Butenes, BPD	10,870	10,870	10,870
Refinery-Grade Propane/Propylene, BPD	0	1500	0
Polymer-Grade Propylene, BPD	0	0	1000

For this study it is assumed that the maximum volume of propylene feed for each case is limited by the following constraints:

- A maximum operating temperature for the existing contactors of 60°F when modified by the addition of tube inserts.
- The capacity of the existing refrigeration compressor case and rotor. The compressor suction pressure is increased consistent with an assumed 60°F contactor temperature limit.
- Segregation of the propylene and butylene feeds to minimize acid consumption. Propylene flows to one Contactor reactor, and the butylene is split evenly between the other three Contactor reactors. Segregation allows each olefin type to be reacted at conditions favorable to that olefin type. For the purposes of this study, the reactors were operated at equal temperatures, but these would be optimized for an actual revamp.
- Acid flows in series with the Contactor reactors starting with the propylene Contactor reactor.
- No revamp scope is required for the effluent wash systems.

Case 1 Results - Refinery grade propylene

Based on the constraints noted above (contactors and refrigeration compressor), it is feasible to add about 1500 BPD of refinery-grade propylene to the feed mix. The composition of the refinery-grade propylene feed is assumed to be:

Component	Vol%
Ethane	0.5
Propene	70.7
Propane	28.4
i-Butane	0.4

Feed System – Case 1

It is assumed that existing storage is available for the refinery-grade propylene. As a conservative approach for the cost estimate, a new feed pump, flow control valve and offsites line are included to feed the alkylation unit. It may be possible to feed the refinery PP's directly from the upstream gas plant depropanizer using the existing pump and a new line to the alkylation unit. New Compabloc Exchangers are added to maximize the BB/PP feeds cooling via exchange with contactor effluent.

Contactor Reactors/Refrigeration Compressor – Case 1

The refinery-grade propylene contains 1060 BPD of propylene that reacts with 1346 BPD of isobutane to produce an incremental 1886 BPD of true alkylate. The exothermic heat of reaction for propylene must be transferred to refrigerant in the contactors thereby increasing the mass flow of vapor to the refrigeration compressor. The mass flow of vapor to the compressor suction is estimated to increase from 262,000 lb/hr in the base case to 304,000 lb/hr. The contactors will be upgraded by the addition of tube inserts to improve heat transfer. This is expected to increase the overall heat transfer coefficient from 40-45 to 50+ btu/hr-°F-hr. On this basis, the contactor temperature is estimated to increase from 49°F to 58°F, and the pressure and temperature of the refrigerant in the tube side of the contactors will increase to keep the actual volume of the vapor produced within the capacity of the existing compressor. The compressor suction pressure increases from the base case of 15.1 psia to 17.5 psia.

The refrigeration compressor will not require modification since the actual volume flow does not change. Because of the higher inlet mass flow, the driver horsepower increases by about 10%, thus a new motor is included in the revamp scope.

The refrigeration recycle pump is replaced to handle the increased volume of refrigerant.

Refrigerant Condenser – Case 1

The increase in the mass flow of refrigerant vapor must be condensed at the compressor discharge pressure of 88 psig. The existing total condenser cannot completely condense the vapor, so it will be used as a partial condenser providing about 80%of the total duty, with a new total condenser providing the remaining 20%. Adding a second condensing stage not only adds condensing capacity, but also produces a depropanizer feed with a higher concentration of propane, which reduces the capital cost and utility consumption of the new depropanizer system. Additionally, the existing refrigerant cooler (just downstream of the existing refrigerant accumulator) will be replaced to accommodate the higher duty associated with cooling the condensed liquids from a higher temperature.

Depropanizer System – Case 1

The base case feed and imported butane streams contain a total of 165 BPD of propane, which is separated from the refrigerant by a small depropanizer. Feed to the depropanizer is 10% of the total condensed refrigerant. The additional feed of 1500 BPD of refinery-grade propylene will contain 426 BPD of propane, which exceeds the capacity of the existing depropanizer, so an entirely new depropanizer system is required. The new system will consist of:

- Depropanizer
- Feed Drum
- Feed Pumps
- Feed Caustic Wash
- Feed Coalescer
- Condenser
- Overhead Accumulator
- Overhead and Reflux Pumps
- Feed/Bottoms Exchanger
- Reboiler
- Bottoms Cooler

The propane purge may be able to be routed back to the FCC gas plant if there is adequate capacity.

Deisobutanizer/Debutanizer – Case 1

The deisobutanizer (DIB) will function adequately without modification. The isobutane recycle rate and concentration remain identical to the base case. The isobutane to olefin volume ratio is reduced from 7.78 to 7.25. This i:O ratio reduction is accounted for in the resulting alkylate property prediction.

The debutanizer will be adequate for the increased rates as long as performance specs are relaxed slightly. It is estimated that the alkylate RVP will increase from 3.7 to 3.9 psia, and the n-butane product purity will be reduced from 90% to 88%.

To account for the higher alkylate flow rate, and as a conservative approach on the cost estimate, the alkylate rundown water cooler is replaced to handle additional duty. In many revamp scenarios, an operator may be able to handle a higher rundown temperature.

Case 2 Results – Polymer Grade Propylene

Based on the contactor/compressor constraints noted previously, it is feasible to add 1000 BPD of polymer-grade propylene to the feed mix. Composition of propylene feed is assumed to be:

Component	Vol%
Ethane	0.05
Propene	99.7
Propane	0.2
i-Butane	0.05

Feed System – Case 2

It is assumed that the purchased polymer-grade propylene will be segregated from the existing refinery propane-propylene in four new bullets sufficient for five days of storage. A new feed pump, flow control valve and offsites line are included in the cost estimate to feed the alkylation unit. Loading facilities for rail or truck are assumed to be existing and adequate for off-loading polymer-grade propylene to the new bullets. New Compabloc exchangers are added to maximize the BB/polymer-grade propylene feed cooling via exchange with contactor effluent.

Contactor Reactors/Refrigeration Compressor – Case 2

The polymer-grade propylene contains 997 BPD of propylene that reacts with 1266 BPD of isobutane to produce an incremental 1774 BPD of true alkylate. The exothermic heat of reaction for propylene must be transferred to refrigerant in the contactors, thereby increasing the mass flow of vapor to the refrigeration compressor. The mass flow of vapor to the compressor suction is estimated to increase from 262,000 lb/hr in the base case to 300,000 lb/hr. The contactors will be upgraded by the addition of tube inserts to improve heat transfer. This is expected to increase the overall heat transfer coefficient from 40-45 to 50+ btu/lb-°F-hr. On this basis, the contactor temperature is estimated to increase from 49°F to 58°F, and the pressure and temperature of the refrigerant in the tube side of the contactors will increase to keep the actual volume of the vapor produced within the capacity of the existing compressor. The compressor suction pressure increases from the base case of 15.1 psia to 17.1 psia.

The refrigeration compressor will not be modified, since the actual volume flow does not change significantly, but it will require a new motor to accommodate a 10% power increase.

The refrigeration recycle pump is replaced to handle the increased volume of refrigerant.

Refrigerant Condenser – Case 2

The increase in mass flow of refrigerant vapor must be condensed at the compressor discharge pressure of about 88 psig. The existing total condenser cannot completely condense the vapor, so it will be used as a partial condenser providing about 80%of the total duty, with a new total condenser providing the remaining 20%. Adding a second condensing stage not only adds condensing capacity, but also produces a depropanizer feed with a higher concentration of propane, which improves the performance of the existing depropanizer system. Additionally, the existing refrigerant cooler (just downstream of the existing refrigerant accumulator) will be replaced to accommodate the higher duty associated with cooling the condensed liquids from a higher temperature.

Depropanizer – Case 2

As noted previously, the base case feed and imported butane streams contain a total of 165 BPD of propane, which is separated from the refrigerant by a small depropanizer. The base case feed to the depropanizer is 10% of the total condensed refrigerant. The additional 1000 BPD of polymer-grade propylene and the incremental purchased isobutane will contain an additional 30 BPD of propane. The existing depropanizer can be reused as long as the compressor discharge partial condenser and additional total condenser are utilized similar to Case 1.

Deisobutanizer/Debutanizer – Case 2

The deisobutanizer will function adequately without modification. The recycle rate and isobutene concentration remain identical to the base case. The isobutane to olefin volume ratio is reduced from 7.78 to 7.30. This i:O ratio reduction is accounted for in the resulting alkylate property prediction.

The debutanizer will also be adequate for the increased rates, as long as performance specs are relaxed slightly. It is estimated that the alkylate RVP will increase from 3.7 to 3.9 psia, and the n-butane purity will be reduced from 90% to 88%.

As with Case 1, to account for the higher alkylate flow rate, the alkylate rundown water cooler is replaced to handle additional duty.

Table 3 shows a comparison of the key process information for each case:

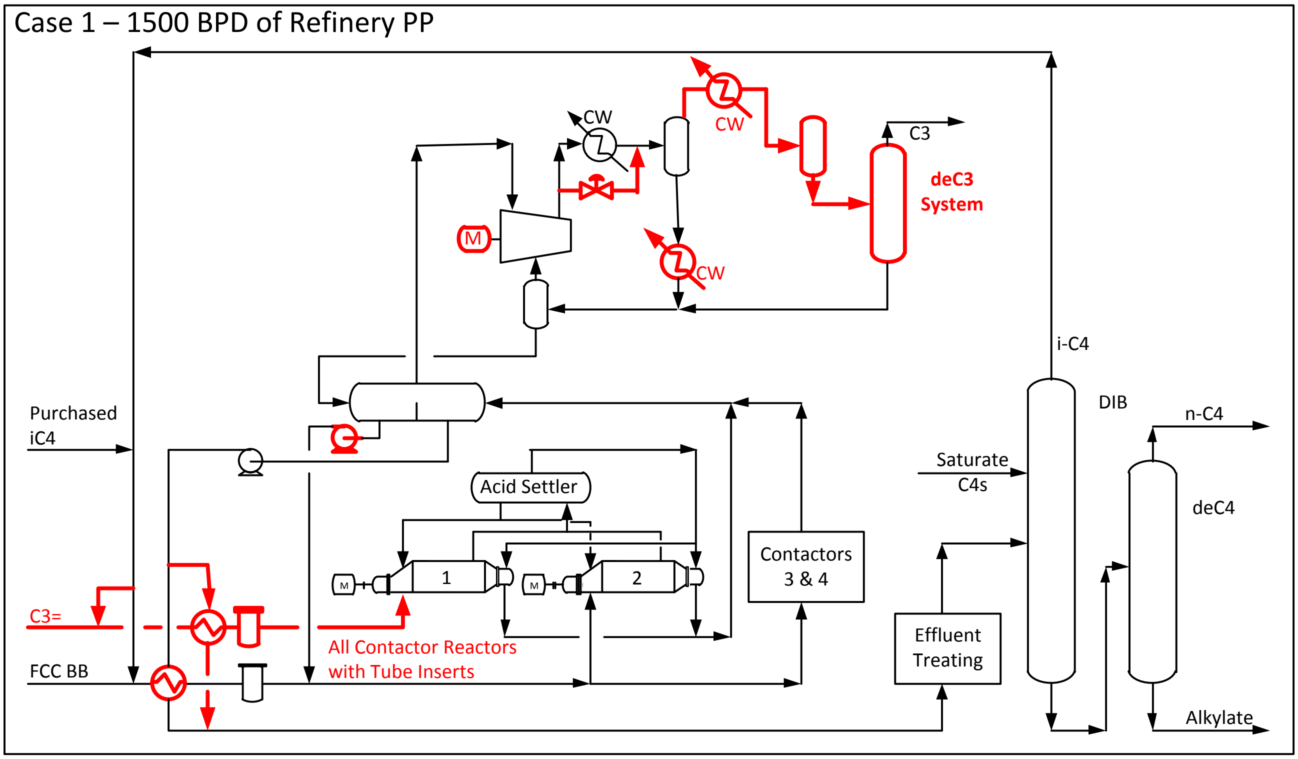
Table 3 – Process Data

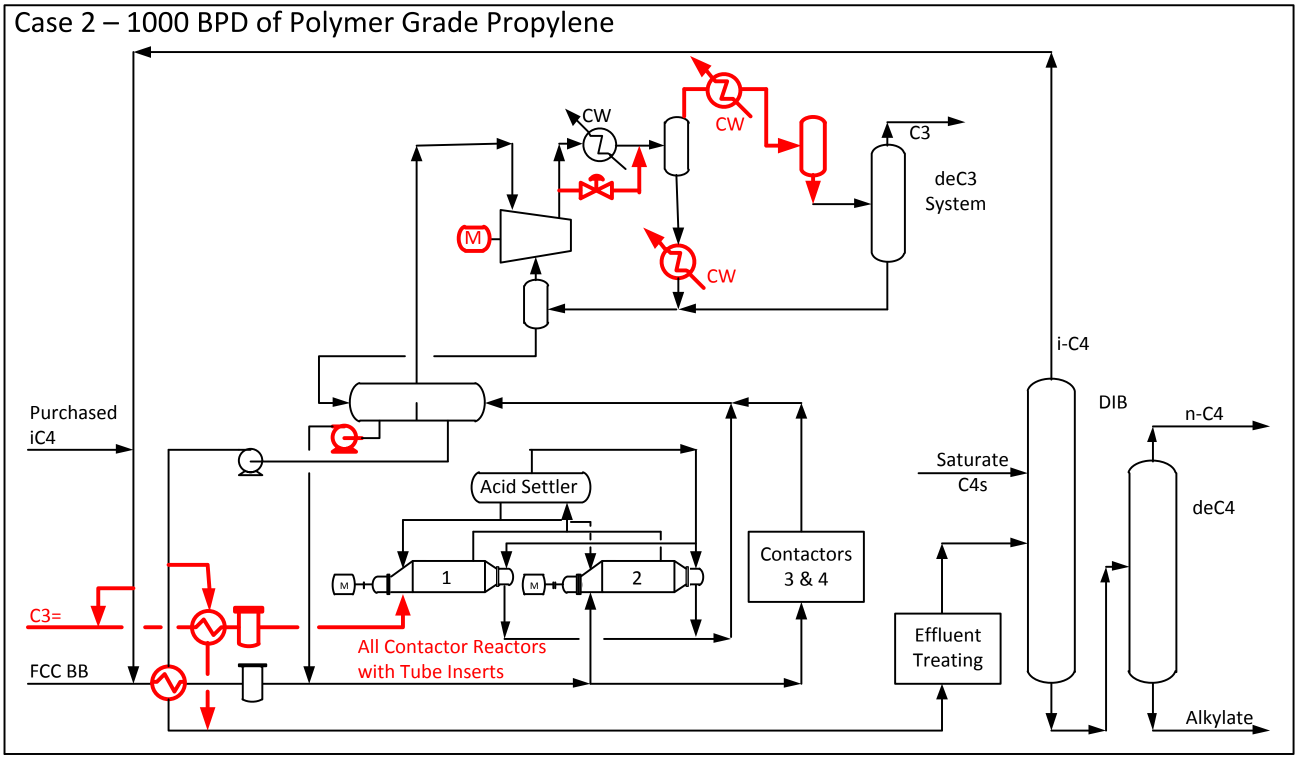
		Base Case	Case 1 Add 1500 BPD Refinery Grade Propylene	Case 2 Add 1000 BPD Polymer Grade Propylene
Refinery BB	BPSD	10870	10870	10870
Refinery PP	BPSD	0	1500	0
Purchased Propylene	BPSD	0	0	1000
Alkylate Product	BPSD	10085	11988	11881
Contactor Temperature	°F	49	58	58
Contactor Pressure	psia	80	80	80
Isobutane Consumption	BPSD	6180	7527	7446
Recycle Isobutane Flow	BPSD	19500	19500	19500
Isobutane from Flash Drum	BPSD	26470	30630	30475
Recycle Isobutane Purity	vol %	85.0	85.0	85.0
Isobutane/Olefin Ratio	vol/vol	7.78	7.25	7.30
Contactor Heat Removal	MMBtu/hr	29.43	34.72	33.95
Reactor Effluent Flow	BPSD	56898	63519	62796
IC4 Vol% in Contactor Effluent	Vol %	66	64	65
Tube-Side Temp In	°F	32.0	39.7	40.2
Tube-Side Temp Out	°F	32.1	42.7	42.2
LMTD	°F	16.9	16.8	16.8
Contactor UA	Btu/(hr*°F)	1,736,393	2,070,658	2,025,665
No. of Contactors		4	4	4
Total Ht. Transfer Area	ft^2	40,280	40,280	40,280
Required 'U'	Btu/(hr*ft^2*°F)	43	51	50
n-Butane in butane product	Vol %	90	88	88
i-Butane in Propane product	Vol%	1.6	1.6	1.6
Alkylate RVP	psia	3.7	3.9	3.9

Alternative Refrigeration Revamp Strategy

In both revamp cases, the increased refrigeration load was handled with the existing compressor with a larger driver to accommodate the increased refrigerant mass flow. An alternative approach, depending on the specifics of the unit, can be to add refrigeration capacity using modular chillers to pre-chill the unit feed and economizer feed streams.

Figures 2 and 3 – The Revamp PFD for each case


Case 1 – 1500 BPD of Refinery PP


Case 2 – 1000 BPD of Polymer Grade Propylene

Financial Analysis

The internal rate of return (IRR) for each of the study cases was calculated based on the estimated total installed cost (TIC) and additional net revenue from producing the additional alkylate and propane products minus the feed and incremental operating costs. This analysis is based on the following assumptions.

- The value of the alkylate product receives the same market-based price for the base and study cases. While lower octane than butane alkylate, propylene-alkylate meets the octane specifications of market-based price quotes.
- Incremental utilities are available
- MCC has spare space for higher horsepower compressor motor
- Space is available for new equipment including the new propylene bullets for Case 2.
- Project life of 15 years
- Corporate tax rate of 35%
- Property tax and insurance on TIC of 3%
- On-stream rate of 97% (40-day shutdown every four years)
- Accelerated depreciation of 10 years
- Pricing for isobutane, refinery and polymer grades of propylene, propane and alkylate are per IHS 2016 projections.

The estimated TIC is 30.0 MM$ and 33.4 MM$ for Case 1 and Case 2 respectively, and the calculated IRR's are 19% and 13%. Table 4 summarizes the economic analysis.

The following sensitivity alternatives were investigated:

- Alkylate and refinery-grade propylene pricing for Case 1 (Figure 4)
- Alkylate and polymer-grade propylene pricing for Case 2 (Figure 5)
- Total installed cost for Cases 1 and 2 (Figure 6)

Table 4 – Summary of Economics

		Base Case	Case 1	Case 2
		Butylene Feed Only	1500 BPD Refinery Grade PP	1000 BPD Polymer Grade C3=
Cash Flow Analysis Summary				
Capital Cost	MM$		30.0	33.4
Earnings before insur and prop tax	MM$/yr		8.68	8.67
NPV at 10% IRR	MM$		15.4	5.6
NPV at 15% IRR	MM$		5.4	-3.3
IRR	%		19%	13%
Acid Consumption				
Acid Consumption C3=	lb bbl/gal alk	-	0.60	0.60
Acid Consumption C4=	lb bbl/gal alk	0.40	0.50	0.50
Alkylate (R+M)/2	Octane #	93.9	92.6	92.6
Feeds				
Imported iC4	BPD mixture	1,955	3,437	3,342
C4= Feed	BPD C4= mix	10,870	10,870	10,870
C4 Saturates	BPD mixture	3,098	3,098	3,098
Refinery PP	BPD mixture		1,500	
Polymer Grade C3=	BPD mixture			1,000
Products				
Propane	BPD	166	639	195
n-Butane	BPD	3,971	4,088	4,076
Alkylate	BPD	10,085	11,988	11,881
Utilities:				
Power, kW	kW	4,988	5,495	5,430
50 psig steam	lb/hr	63,080	73,912	66,213
150 psig steam	lb/hr	11,924	12,437	12,380
Cooling water	gpm	6,563	10,270	8,502
Wash water	gpm	40	47	47
Chemicals:				
Sulfuric Acid	Ton/Day	85	130	128
Caustic	Ton/Day	0.58	0.68	0.68
Total Gross income	$/day	1,183,155	1,395,975	1,368,073
Total Costs	$/day	120,707	309,005	281,124
Net Income	$/day	1,062,448	1,086,970	1,086,949
Delta Total Gross income	$/day	0	212,820	184,918
Delta Total Costs	$/day	0	188,299	160,417
Delta Net Income	$/day	0	24,522	24,501
Delta Net Income /cal yr	$/yr		8,950,433	8,942,783
Onstream factor			0.97	0.97
Delta Net Inc/yr * onstrm fctr	$/yr		8,681,920	8,674,500

Figure 4

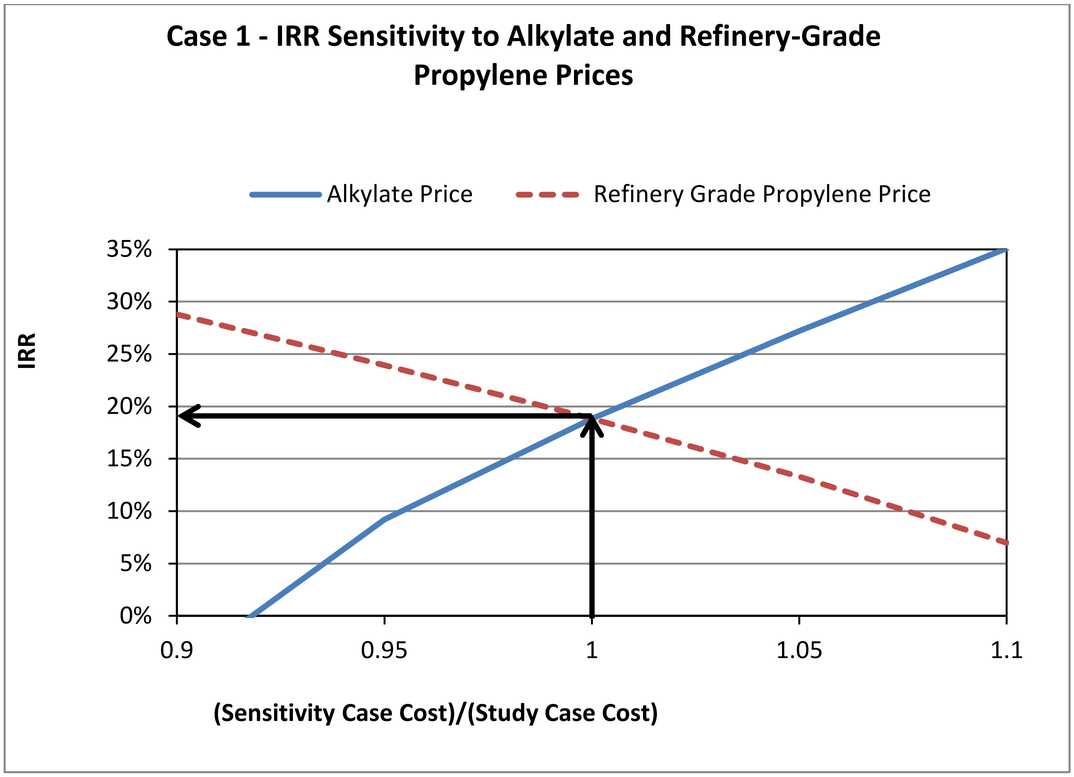


Figure 5

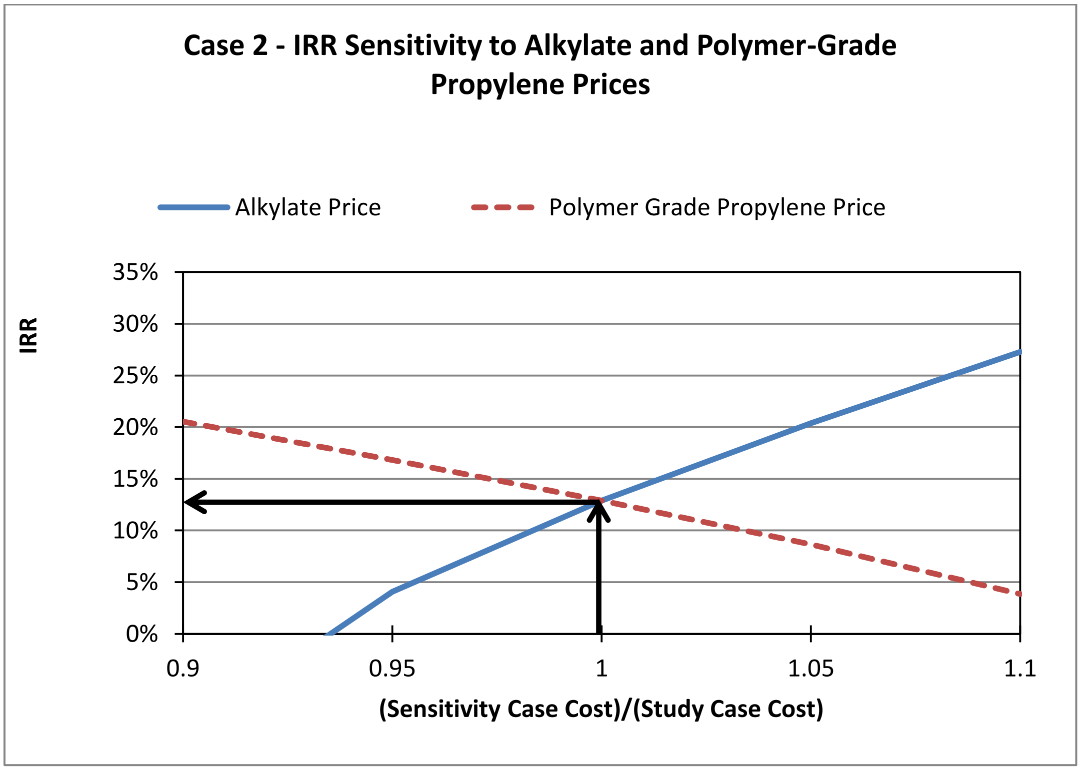
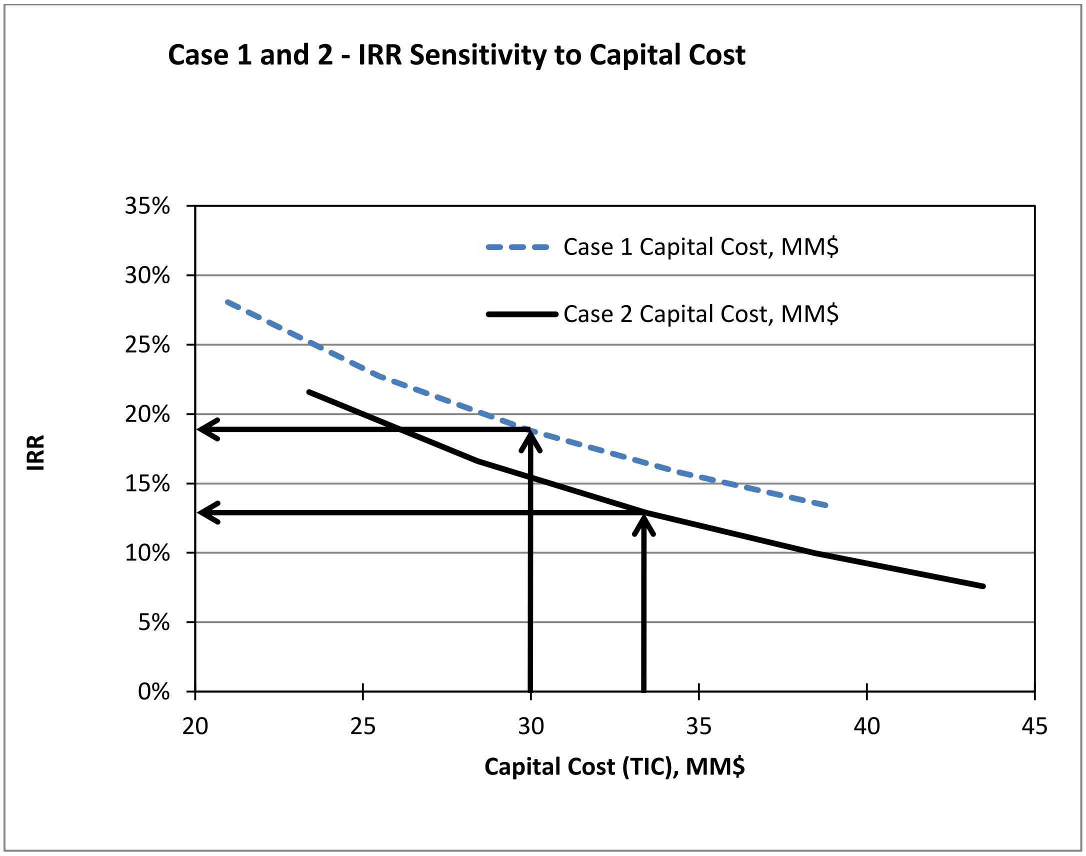


Figure 6



Conclusions

This study shows that, for a modest investment, the production of alkylate from an existing, butylene alkylation unit can be increased by over 10% with the addition of propylene to the feed. The calculated rate of return, however, is marginal based on the feed and product prices used for the study. For either case (refinery- or polymer-grade feed), the economics are very sensitive to feed and product pricing. If the alkylate value increases by 10%, the IRR nearly doubles, while an increase of the same magnitude in feed (propylene) cost reduces the IRR by about 50%. For Case 1, the IRR decreases to 14% for a 25% increase in the TIC. For a 25% decrease in the TIC the IRR improves to 26%. For Case 2 the IRR is reduced to 8% for a 25% increase in the TIC and improves to 20% for a 25% TIC reduction. For Case 2 the quantity, and thus investment, of new storage required for polymer-grade propylene significantly impacts the TIC and thus the economics.

There are some uncertainties associated with the production of incremental alkylate from a US refinery. The continuation of high-octane values is uncertain as lower oil prices affect the incremental economics of naphtha reforming and ethanol blending requirements continue under the Renewable Fuel Standard. Also, US gasoline demand will continue to decrease in the future because of Corporate Average Fuel Economy (CAFE) rules. Nevertheless, alkylation has historically been a fix for several blending constraints – aromatics, octane, sulfur and RVP, and there will continue to be significant opportunities to export gasoline to Latin America, especially from the US Gulf Coast for the foreseeable future. In cases where increased yields of light naphtha from new US light crude (LTO) production are absorbed in a refinery gasoline pool, more octane barrels will be required. Also, the heavy naphthas from these crudes are lower quality and result in reduced reformate yields. Further, it is anticipated that higher octanes will be required for future car engines to meet CAFE standards. Therefore, increasing alkylation capacity by processing propylene may be attractive for some refineries.

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Biography for Mr. Julian Migliavacca

Mr. Migliavacca is a Process Engineering Manager who works within the Downstream Process Engineering group as part of the Process Plants and Industrial business unit. He has been a dedicated and valued part of the Wood Group Mustang team for the past 16 years.

His valued experience ranges from grass roots refinery studies to detail design of refinery process units. Mr. Migliavacca’s refining experience includes crude and vacuum units, gasoline and diesel hydrotreating, alkylation, catalytic reforming, and delayed coking. He holds a BSChE degree from the University of Texas at Austin.